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7. Author(s) Richard E. Lyon[1], Lauren M. Castelli[2], and Richard Walters[3]		8. Performing Organization Report No.
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16. Abstract

The flammability, thermomechanical properties, and fire response of the diglycidylether of 1,1-dichloro-2,2-bis(4-hydroxyphenyl)ethylene (DGEBC) cured with several hardeners were examined and compared to diglycidylether of bisphenol-A (DGEBA) systems. The DGEBC and DGEBA were cured with (1) triethylenetetramine, (2) methylenedianiline, (3) the parent phenol (BPC or BPA), (4) catalytic amounts of (2-ethyl-4-methylimidazole) (EMI-24), and (5) the dicyanate of bisphenol-C. Cured samples were measured for strength, modulus, flame resistance (limiting oxygen index (LOI), UL-94 V), flaming heat release rate, and heat release capacity. The mechanical properties of the DGEBC and DGEBA systems were equivalent but the DGEBC systems exhibited superior flame resistance and 50% lower heat release rate and heat release capacity than the corresponding DGEBA system. The DGEBC cured with methylenedianiline had an LOI of 30-31, exhibited UL 94 V-0/5V behavior and easily passed the Federal Aviation Administration heat release requirement Federal Aviation Regulation 25.853 (a-1) as a single-ply glass fabric lamina.

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EXECUTIVE SUMMARY

The flammability, thermomechanical properties, and fire response of the diglycidylether of 1,1-dichloro-2,2-bis(4-hydroxyphenyl)ethylene (DGEBC) cured with several hardeners were examined and compared to diglycidylether of bisphenol-A (DGEBA) systems. The DGEBC and DGEBA were cured with (1) triethylenetetramine, (2) methylenedianiline, (3) the parent phenol (BPC or BPA), (4) catalytic amounts of (2-ethyl-4-methylimidazole) (EMI-24), and (5) the dicyanate of bisphenol-C. Cured samples were measured for strength, modulus, flame resistance (limiting oxygen index (LOI), UL-94 V), flaming heat release rate, and heat release capacity. The mechanical properties of the DGEBC and DGEBA systems were equivalent but the DGEBC systems exhibited superior flame resistance and 50% lower heat release rate and heat release capacity than the corresponding DGEBA system. The DGEBC cured with methylenedianiline had an LOI of 30-31, exhibited UL 94 V-0/5V behavior and easily passed the Federal Aviation Administration heat release requirement Federal Aviation Regulation 25.853 (a-1) as a single-ply glass fabric lamina.

Until the mid-1980s, epoxy resins were widely used in aircraft cabin interiors as a matrix for fiber-reinforced composite honeycomb sandwich panels because of the facile solvent-free processing, good mechanical properties and adhesion, and the high surface quality made possible by the addition cure reaction. In 1990, the Federal Aviation Administration (FAA) enacted regulations limiting the rate of heat released and smoke emissions by aircraft interior panels in flaming combustion [1]. Conventional epoxies could not pass the new FAA heat release rate and smoke emissions requirement, which forced the aircraft industry to switch to more fire-resistant thermoset resins such as phenol-formaldehyde condensation polymers (phenolics) for interior panel construction. Phenolic resins have drawbacks, however, as a matrix for aircraft interior decorative panels [2]. In particular, phenolics are not as strong or tough as epoxies, have poor tack and drape, and contain residual formaldehyde (a human carcinogen) so that lay-up must be performed under well-ventilated conditions. Moreover, the condensation reactions that produce the phenolic network liberate water which vaporizes at cure temperatures and forms voids in the resin during fabrication. Voids cause surface roughness which weakens the composite, reduces adhesion to surface films and honeycomb, and therefore must be corrected by labor-intensive (i.e., costly), sand-and-sweep operations. Consequently, ultra-low heat release, addition cure, thermoset polymers are of potential interest to the aircraft industry in general and the FAA in particular [3].

In the 1960s and 70s, novel, fire-resistant, thermoplastic polymers and thermoset resins derived from 1,1,1-trichloro-2,2-bis(4-hydroxyphenyl)ethane (I) and its dehydrochlorination product 1,1,-dichloro-2,2-bis(4-hydroxyphenyl)ethylene (II) were reported by Russian and Polish researchers [4] (see figure 1). Epoxies were among the thermoset resins that were synthesized from these chlorobisphenols [5-9] and, when cured with conventional hardeners, the epoxies exhibited self-extinguishing behavior in flame tests and the mechanical properties were equivalent to the bisphenol-A epoxy analogs. Synthesis of the diglycidylether of bisphenol C (II) is accomplished in a three step, environmentally-friendly process yielding only HCl and water as byproducts, as shown in figure 1. The first step involves reacting two moles of phenol with one mole of chloral under strongly acidic conditions [10] to give compound I, followed by recrystallization and subsequent dehydrochlorination [11] to give compound II, 1,1-dichloro-2,2-bis(4-hydroxyphenyl)ethylene (bisphenol from chloral, bisphenol C, BPC), melting point 217° ±2°C. Reaction of bisphenol C with two moles of epichlorhydrin [5-9] gives the crystalline diglycidylether of bisphenol C (III), melting point 91° ±5°C.

Over the past two decades, since the flammability of chlorobisphenol epoxies was evaluated, it has been established that self-extinguishing behavior in an isolated flame test [12 and 13] is a poor predictor of material fire hazard in a radiant heat environment (i.e., a fire). A better indicator of a fire hazard is the rate of heat released by a material in forced, flaming combustion [14], and new test methods have been developed to measure flaming heat release and heat release rate in a radiant heat environment [15 and 16]. The FAA is evaluating the fire hazard of chlorobisphenol resins using modern fire performance test methods (e.g., heat release rate in flaming combustion and pyrolysis combustion flow calorimetry) as part of an ongoing effort to identify cost-effective, zero heat release rate materials for next generation aircraft cabin interiors [3].

2 HO—⬡ (Phenol) + H—C(=O)—C(Cl)(Cl)—Cl (Chloral) $\xrightarrow[-H_2O]{H^+}$ HO—⬡—C(CCl_3)(H)—⬡—OH (**I**)

I $\xrightarrow{-HCl}$

2 H_2C(O)CH—CH_2-Cl (Epichlorohydrin) + [from **I**] $\xrightarrow{-2\ HCl}$

HO—⬡—C(=CCl_2)—⬡—OH   Bisphenol C (BPC) **II**

H_2C(O)CH—CH_2—O—⬡—C(=CCl_2)—⬡—O—CH_2-CH(O)CH_2

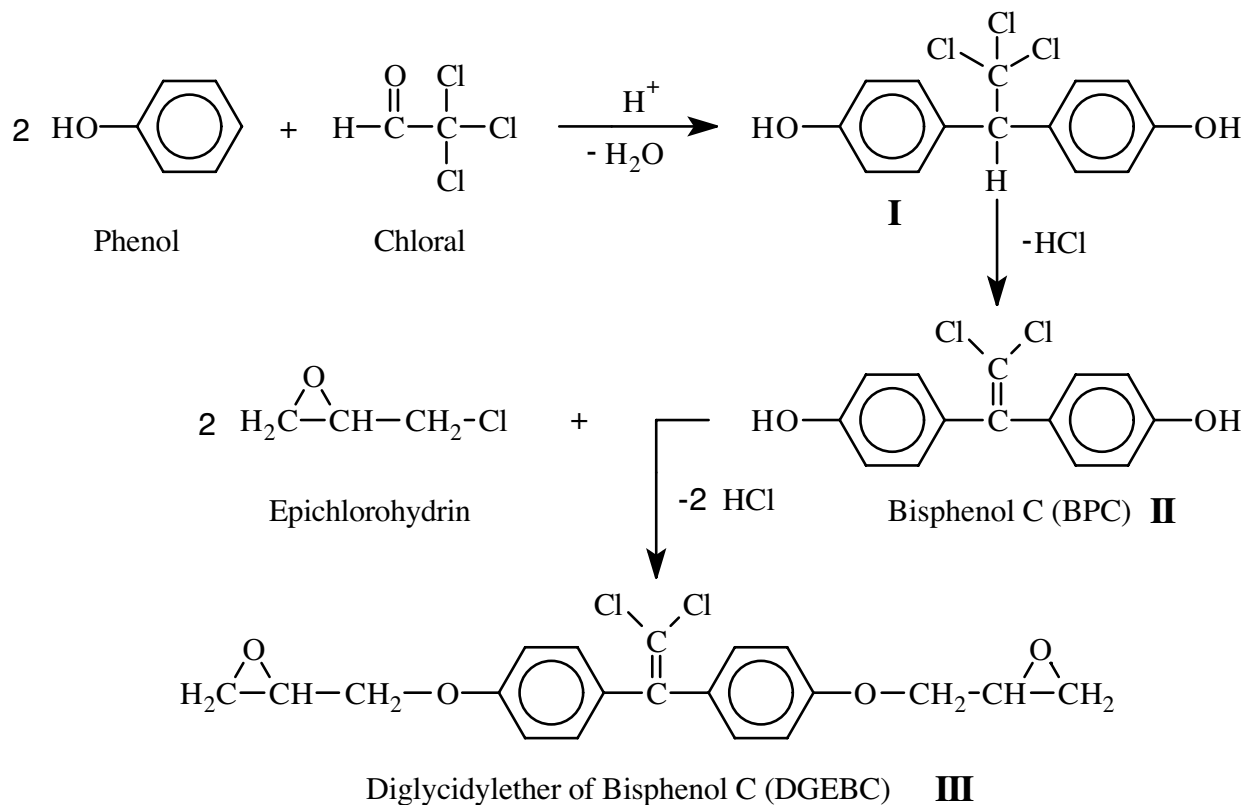Diglycidylether of Bisphenol C (DGEBC) **III**

FIGURE 1. SYNTHESIS OF DGEBC

This study examines the fire, flammability, thermal, and mechanical properties of DGEBC and DGEBA epoxies polymerized by four different mechanisms: (1) anionic ring opening polymerization using catalytic amounts of 2-ethyl-4-methylimidazole; (2) addition polymerization with aliphatic (triethylenetetramine) and aromatic (4,4'-methylenedianiline) amines; (3) catalyzed phenolic cure with the parent phenols (bisphenols A and C); and (4) the dicyanate ester resin derived from bisphenol C.

EXPERIMENTAL

MATERIALS.

The DGEBC and DGEBA epoxy resins and all of the hardeners (see table 1) were technical grade purity ($\geq$ 97%) and were used as received from the manufacturers or suppliers without further purification. The triphenylphosphine (TPP) (99%) [CAS Reg. No. 603-35-0], used as a catalyst for the epoxy-phenol cure reaction, was obtained from Aldrich Chemical Co., Inc. The diglycidyl ether of bisphenol C (DGEBC) epoxide equivalent weight (EEW) was determined to be 209g/eq (formula weight 197 g/eq), with a Brookfield viscosity at 75°C of 460 centipoise, a Gardener color of 9, a hydrolyzable chlorine of 0.101%, and a density of 1.32 g/cm^3. The diglycidyl ether of bisphenol A (DGEBA) had EEW 172 g/eq, with a Brookfield viscosity at 25°C of 5,065 centipoises, a Gardener color 13, a hydrolyzable chlorine of 0.02%, and a density of 1.16 g/cm^3.

TABLE 1. RESINS AND HARDENERS

	Trade Name [CAS Registry No.]	Supplier	Equiv. Weight (g/eq)
Epoxy Resins			
diglycidylether of bisphenol-A (DGEBA)	DER-322 [001675-54-3]	Dow Chemical	174
diglycidylether of bisphenol-C (DGEBC)	RD-98-238 [N/A]	Ciba Specialty Chemicals	208
	XPR-1015 [N/A]	Pacific Epoxy Polymers	209
Hardeners			
2-ethyl-4 methyl-imidazole (2,4-EMI)	Imicure 24 [931-36-2]	Air Products and Chemicals	N/A
triethylenetetramine (TETA)	DEH-24 [000112-24-3]	Dow Chemical	24
4,4'-methylenedianiline (MDA)	Curithane 103 [101-77-9]	Acros	102
4,4'-isopropylidenediphenol (BPA)	Bisphenol A [80-05-7]	Sigma Chemical	114
1,1-dichloro-2,2-bis(4-hydroxyphenyl)ethylene (BPC)	Bisphenol C RD98-237 [14868-03-2]	Ciba Specialty Chemical	141
cyanate ester of bisphenol-C (CEBPC)	RD-98-228 [N/A]	Ciba Specialty Chemical	165

SAMPLE PREPARATION.

Epoxies (DGEBA and DGEBC) were warmed to melting and the curing agents added and mixed until homogeneous. The resin-hardener mixture was then poured into preheated molds and cured in a forced convection oven to make thermal, mechanical, and flammability test samples or was hand impregnated into E-glass fabric (0.22-mm-thick 6781 S. Glass "Griege" weave 8HS 8.95 oz/sq yd, BGF Industries Inc.) and cured in a Carver press under contact pressure to make single-ply glass lamina for heat release rate testing in the FAA fire calorimeter. The formulations and cure schedules were as follows:

- 2-Ethyl-4-methyl imidazole. Two parts by weight of EMI-24 per hundred parts resin (phr) was added to each of the DGEBA and DGEBC epoxies and samples were cured at 100°C for 16 hrs and 150°C for 2 hours.

- Triethylenetetramine. DEH-24 was added to DGEBA (14.0 phr) and DGEBC (13.5 phr) at 85°C and the samples cured in an oven at 50°C for 16 hours followed by 3 hours at 150°C.

- 4,4'-Methylenedianiline. MDA was added to DGEBA (58.6 phr) and DGEBC (56.4 phr) and samples cured at 100°C for 16 hours, 125°C for 2 hours, and 175°C for 16 hours.

- Bisphenols A and C. Bisphenol A (66 phr) was added to DGEBA with 2% triphenylphosphine catalyst. Bisphenol C (78 phr) was added to DGEBC epoxy and 2% w/w triphenylphosphine was added as a catalyst. Both formulations were cured 16 hours at 150°C and 24 hours at 200°C.

- Cyanate ester of bisphenol C. The cyanate ester of bisphenol C (CEBPC) was added at 40 mole percent (53 phr) to the DBEBC epoxy and cured for 1 hour at 100°C and 16 hours at 175°C.

TEST METHODS.

The following methods were used to evaluate the flammability, fire behavior, thermal transitions, and mechanical properties of the DGEBA and DGEBC systems.

- Extent of Reaction. Complete reaction (cure) was confirmed for each formulation and cure schedule using near infrared spectroscopy (Nicolet Magna 550 FTIR) to monitor the disappearance of the CH overtone band of the epoxide at 4535 cm^{-1} [17 and 18].

- Heat of Polymerization. A differential scanning calorimeter (Perkin-Elmer DSC-7) was used to determine the heat of polymerization ΔH_{polym} at a heating rate of 10°C/min under nitrogen.

- Thermal Stability. The temperature at peak mass loss rate (T_p) and char fraction (μ) were measured in a thermogravimetric analyzer (Perkin Elmer TGA-7) using 5-mg samples and a constant heating rate of 10°C/min from 100° to 900°C under nitrogen.

- Dynamic Combustion Potential. The heat release capacity [19] is a quantitative measure of the dynamic combustion potential of a material and is a good predictor of fire and flame test performance. The heat release capacity was measured in a pyrolysis-combustion flow calorimeter (PCFC) [20 and 21]. The PCFC is a thermoanalytical technique that reproduces the separate processes of fuel generation and combustion as they occur at the material surface in a fire. In the test, a 1-milligram sample is placed inside a quartz capillary tube and heated to 900°C in an inert gas stream (nitrogen) at a constant heating rate ≤ 5 K/s. The fuel gases are swept from the pyrolyzer by the nitrogen purge gas, mixed with excess oxygen, and enter a tubular furnace at 900°C where complete oxidation of the fuel occurs. The (nonflaming) combustion products (water, carbon dioxide, and possibly acid gases) are removed from the gas stream by Ascarite™ and Drierite™ scrubbers and the mass flowrate and oxygen concentration are measured and used to calculate the heat release rate of the sample from the oxygen consumption [22]. Dividing the maximum value of the heat release rate (W) by the initial sample mass (g) and heating rate (K/s) gives the heat release capacity (η_c) of the sample in units of J/g-K.

- Ignition Resistance. The propensity for upward vertical burning in the absence of external radiant heat was measured according to the UL-94 V standard test method [12] using rectangular bars measuring 3 by 13 by 76 mm. The minimum concentration of oxygen (v/v) which would support candle-like burning in the absence of external radiant heat, or limiting oxygen index (LOI), was determined according to the standard test method [13] using rectangular bars measuring 125 by 6.5 by 3 mm.

- Fire Calorimetry. The Ohio State University Rate of Heat Release Apparatus [23] was used to measure the heat release rate and heat released in forced flaming combustion of epoxy-glass lamina at an external radiant heat flux of 35 kW/m^2 according to Federal Aviation Regulations (FAR) 25.853 (a-1). Duplicate epoxy-glass lamina having approximate dimensions 150 by 150 by 0.23 mm were tested for each formulation.

- Glass Transition Temperature. Dynamic torsion testing (Rheometrics RDA II) was used to measure the glass transition temperature (T_g) and shear storage modulus (G′) of rectangular bars measuring 20 by 13 mm with a thickness of 1-6 mm. Samples were heated at a constant rate of 5ºC/min between 25º and 250ºC at a frequency of 1 Hz. The glass transition temperature was assigned to the temperature at which the tangent to the phase angle (tan Δ) was a maximum.

- Compressive Properties. Compressive modulus and yield stress were measured in triplicate according to standard procedures [24] on a universal testing machine (INSTRON 4400-R Model 1125) at crosshead speed of 1.3 mm/min using 5.5-mm-diameter, right circular cylinders which were 17 mm long. The compliance-corrected load versus time data was used in the calculations.

RESULTS AND DISCUSSION

Table 2 lists the heats of polymerization per mole of epoxide, ΔH_{polym}, obtained by DSC, as well as the decomposition temperature, T_p, and char yield, μ, of the epoxy formulations obtained by thermogravimetric analysis (TGA). Also listed in table 2 are the heat release capacity, η_c, heat of combustion of the fuel gases per original mass of polymer, h_c, and pyrolysis residue, μ, at 900°C obtained by PCFC. The measured exothermic heat of polymerization of the DGEBC and DGEBA per mole of epoxide group is $\Delta H_{polym} = 86 \pm 13$ kJ/mol for the EMI, TETA, MDA, and BPA/BPC hardeners. This value is in the range $\Delta H_{polym} = 106 \pm 20$ kJ/mol [18] reported for epoxide reactions. The heat of polymerization of the CEBPC hardener, $\Delta H_{polym} = 120$ kJ/mole-epoxide, is significantly higher than for the other hardeners because of the heat liberated by the cyclotrimerization reaction of the cyanate ester to form the cyanurate ring and the subsequent cyanurate-epoxy reaction to form the oxazoline [25]. Another method described by Bauer [26] suggests a rearrangement of the cyanurate to the isocyanurate followed by its cleavage and subsequent reaction with the glycidylether to form an oxazolidone.

TABLE 2. THERMAL ANALYSIS RESULTS

Hardener	Epoxy DGEB	DSC ΔH_{polym} (kJ/mol)	TGA T_p (°C)	μ (%)	PCFC η_c (J/g-K)	h_c (kJ/g)	μ (%)
EMI-24	A	72	460	11	833	25	5
	C	83	420	44	487	10	36
TETA	A	92	400	8	655	26	4
	C	78	350	30	577	15	23
MDA	A	94	425	18	641	26	8
	C	111	310	39	261	16	32
BPA	A	83	450	10	858	27	1
BPC	C	76	330	44	153	11	39
CEBPC	C	120	350	47	291	8	42

Figure 2 shows thermogravimetric data for the DGEBA and DGEBC epoxies cured with MDA. The principle mass loss event for the DGEBC-MDA system begins at a lower temperature than for the DGEBA-MDA system but continues over a much broader temperature range and more char is produced.

Table 2 shows that lower thermal stability (T_p), lower heat of combustion of the fuel gases (h_c), and higher char yield (μ) are characteristic of the DGEBC materials relative to DGEBA. High char yields ($\geq$ 30%, w/w) are usually associated with thermally stable aromatic structures in the polymer backbone. In the case of the DGEBC systems, these aromatic structures are generated in situ as a product of the unique thermal degradation chemistry of the dichloroethylidene linkage. Reasonably good agreement between the TGA and PCFC char yields, μ, is observed despite the weighing error associated with removing the sample from the PCFC apparatus to make the measurement. The DGEBC systems had consistently lower heat release capacities, η_c, and total heat release, h_c, than did the DGEBA systems.
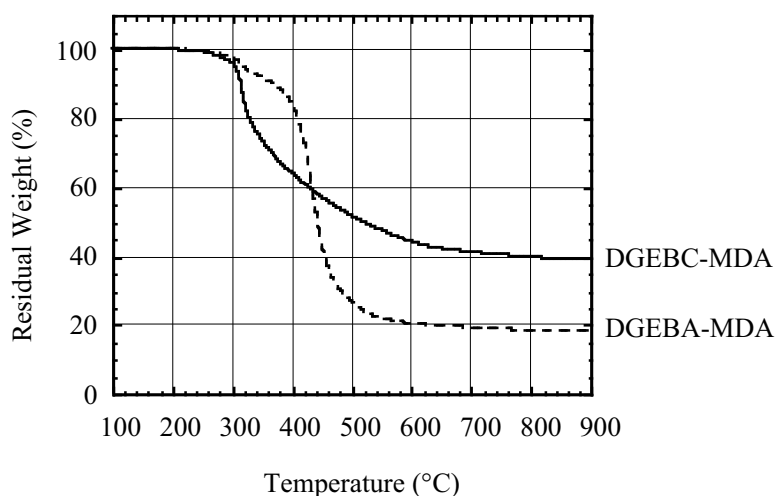

FIGURE 2. THERMOGRAVIMETRY DATA FOR DGEBA-MDA AND
DGEBC-MDA SYSTEMS

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Figure 3 shows a proposed decomposition mechanism of the DGEBC materials [27]. Thermal degradation is thought to proceed via a dichlorostilbene intermediate to yield two moles of hydrochloric acid and diphenylacetylene in the polymer backbone. The diphenylacetylene undergoes a strong exothermic reaction, $\Delta H = 75$ kJ/mole, [27-29] liberating fuel gases R and forming a solid polyaromatic char in near-quantitative yield. According to this degradation scheme, the only volatile degradation products are the noncombustible mineral acid HCl and the R group linking the dichloroethylidene moiety to the polymer backbone. Consequently, the fuel value of the polymer is determined by the heat of combustion of the R group and its tendency to volatilize in a fire.
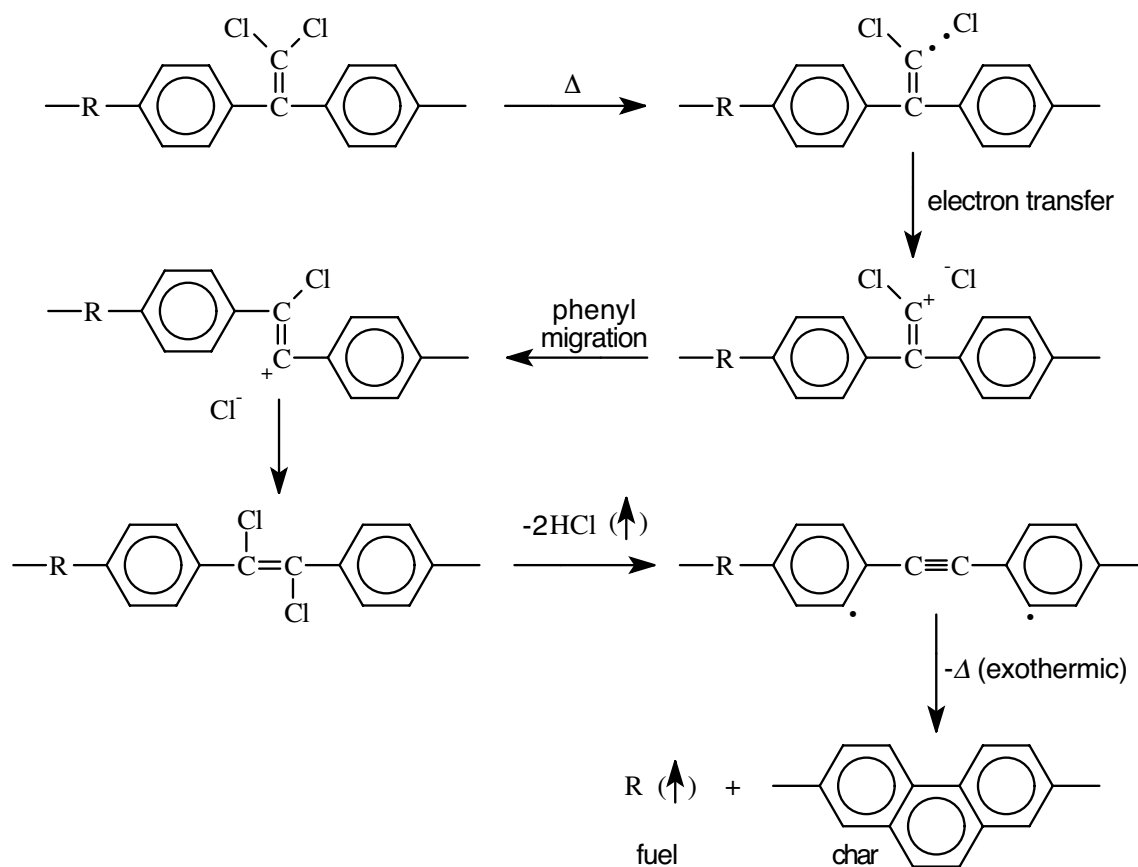

FIGURE 3. THERMAL DEGRADATION MECHANISM OF CHLORAL-BASED
CONDENSATION POLYMERS

It has been found that when the backbone R group has a low heat of combustion such as when R= carbonate [11] or cyanate [25 and 27] or is readily incorporated in the char, e.g., R= phthalate [11], the heat release rate and flammability of the polymer is greatly reduced. In the present case, R is the reaction product of the glycidyl ether with itself (EMI-24 cure), an aliphatic amine (TETA), aromatic amine (MDA), bisphenol (A or C), or the dicyanate ester (CEBPC), so the fuel value of the decomposition products should be equal to the heat of combustion of the volatile fraction of these groups. The data in table 2 is consistent with the thermodynamics of the proposed dichloroethylidene degradation mechanism in that both the char yield, μ, and the measured heat of combustion of the fuel gases, h_c, per unit initial mass of compound are roughly

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equal to the values calculated from the aliphatic portions of the molecule not contained in the dichlorethylidene moiety. By way of example, the R groups for the DGEBC reaction with bisphenol C (R = $C_3H_6O_3$) and EMI-24 (R = $C_3H_5O_2$), which differ only by a hydroxyl (–OH), are shown in figure 4(a) and 4(b) enclosed in the dashed lines. Assuming the volatile fuel compositions are R = $C_3H_6O_3$ and R = $C_3H_5O_2$ for the DGEBC-BPC and DGEBC-EMI systems, respectively, the calculated heats of combustion and char yields are $h_c \approx 7$ kJ/g-compound and $\mu \approx 35\text{-}40\%$, in qualitative agreement with the measured values listed table 2. The backbone phenyl groups of the methyenedianiline hardener are largely incorporated into the DGEBC-MDA char as deduced from the fact that the experimental char yield ($\mu = 39\%$) is significantly higher than the theoretical value calculated assuming a volatile aliphatic glycidylamine fuel group ($\mu = 28\%$).
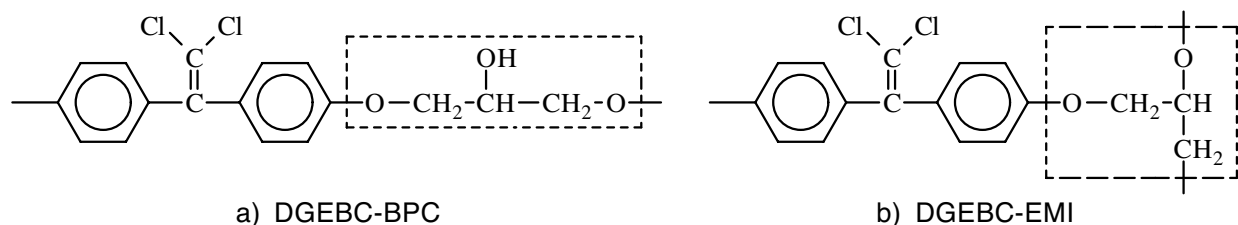

a) DGEBC-BPC   b) DGEBC-EMI

FIGURE 4. IDEALIZED CHEMICAL STRUCTURE OF DGEBC REACTION
PRODUCTS WITH (a) BPC AND (b) EMI (Potentially volatile
fuel component (R group) enclosed in dashes.)

The presence of the hydroxyl group in the phenolic (BPC) cure lowers the heat release capacity and flaming heat release rate (see table 3) of the epoxies relative to the ring-opening polymerization (EMI-24) cure mechanism, possibly as a result of dehydration and transient cross-linking reactions of the hydroxyl group at high temperature. The thermal stability (T_p) of the dichloroethylidene moiety in the amine- and phenolic-cure DGEBC systems is 50°C lower than for the DGEBC-EMI chain homopolymerization ($T_p = 420°C$ in table 2) or linear BPC-based thermoplastics, e.g., BPC-polycarbonate, $T_p \approx 450°C$ [11 and 27-29]. The lowered thermal stability of the dichloroethylidene moiety in the addition-cured systems is due to the presence of hydrogen atoms in unreacted phenol, amine, or hydroxyl groups (bond dissociation energy ≈ 360–430 kJ/mol) [30], which are more labile than the aromatic ring hydrogen (bond dissociation energy ≈ 464 kJ/mol) [30] of the backbone phenyl groups. The labile hydrogen in the addition-cured DGEBC facilitates HCl elimination by the dichloroethylidene moiety so that the major mass loss event occurs at lower temperatures, i.e., $T_p \approx 350°C$ versus $T_p \approx 450°C$ for the linear thermoplastic BPC-polycarbonate.

Table 3 lists the UL 94 V ranking, LOI, peak heat release rate, and total heat release in flaming combustion according to FAR 25.853(a-1).

TABLE 3. FIRE AND FLAMMABILITY DATA

Hardener	Epoxy DGEB	Peak Heat Release Rate (kW/m^2)	Total Heat Release $(kW\text{-}min/m^2)$	LOI $(\% O_2)$	UL 94
EMI-24	A	109	42	19-20	B
	C	50	26	27-28	B
TETA	A	144	67	21-22	B
	C	70	32	—	—
MDA	A	82	46	27-28	B
	C	44	32	—	V-0
BPA	A	71	49	20-22	B
BPC	C	30	19	35-36	V-0
CEBPC	C	34	18	—	—

Thermal and mechanical properties of the DGEBA and DGEBC systems are listed in table 4. Due to limited quantities of DGEBC available, the compressive moduli and strength could not be determined for CEBPC-cured systems, while the compressive properties of the DGEBA-BPA and DGEBC-BPC systems were not tested because of poor sample quality. However, table 4 shows that the glass transition temperatures, shear moduli, and Young's moduli of the DGEBC systems tested are similar to their DGEBA analogs and typical of epoxies in general [17 and 18].

TABLE 4. THERMOMECHANICAL PROPERTIES

Hardener	Epoxy DGEB	Glass Transition Temperature, T_g (°C)	Shear Modulus (GPa)	Young's Modulus (GPa)	Yield Strength (MPa)
EMI-24	A	113	1.10	2.08	111
	C	122	1.10	1.95	123
TETA	A	131	1.15	1.73	107
	C	87	0.82	2.01	96
MDA	A	112	1.25	2.52	118
	C	110	1.38	2.71	123
BPA	A	105	1.05	—	—
BPC	C	—	—	—	—
CEBPC	C	206	—	—	—

CONCLUSIONS

The fire behavior and flammability of an epoxy resin derived from 1,1-dichloro-2,2-bis(4-hydroxyphenyl)ethylene (i.e., diglycidylether of bisphenol-C, DGEBC) was measured and found to be significantly better than bisphenol-A epoxy for each of the five systems compared in the study. All but one of the DGEBC systems passed the FAA requirement for the maximum heat release of large-area aircraft cabin materials FAR 25.853(a-1) and exhibited UL 94 V-0 behavior

with aromatic (MDA and BPC) hardeners. By way of comparison, none of the DGEBA systems passed the FAA heat release requirement or exhibited self-extinguishing characteristics in the UL 94 V test. The thermal and mechanical properties of DGEBC and DGEBA systems were virtually identical.

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